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Setting the trap

How FCC operational flexibility and enhanced optimisation can be achieved with a metals trapping additive.

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Fluidised catalytic cracking (FCC) feed contaminants are a common problem facing most FCC unit (FCCU) operators. Metals, such as vanadium, calcium, nickel, iron, sodium, and potassium, enter the unit with the feed and cause catalyst poisoning through several different mechanisms. The result of this poisoning generally causes an increase in delta coke, which results in: loss of conversion, increased slurry yield, and increased dry gas production.

There are several commonly used ways to attempt to mitigate metals poisoning including increasing fresh catalyst addition rate, adding flushing equilibrium catalyst (Ecat), or incorporating a metals trap into the fresh catalyst. Recent technology advances have created a more effective option for dealing with feed contaminants. Johnson Matthey has created an FCC additive specifically designed for trapping unwanted metals. As a result of this trapping, many positive operating impacts are achieved. This article discusses Parkland Fuel Corp.'s experience with this additive at its refinery in Burnaby, Canada, and the various ways they took advantage of the benefits attained.

Burnaby refinery

The FCCU at Parkland's Burnaby refinery processes a feed containing 60% atmospheric tower bottoms (ATBs) and 40% vacuum gas oil (VGO). The feed has a very high vanadium content ranging from 12 to 19 ppm. The vanadium level is dependent on crude type and FCC feed cut point. Inside the regenerator, the feed vanadium forms vanadic acid (H_3VO_4), which is very destructive to the FCC catalyst zeolite. In addition, vanadium promotes dehydrogenation reactions which increase hydrogen to the wet gas compressor.

The feed is also rich in iron resulting in Ecat iron ranging from 0.8 to 1.1 wt%. At such high levels, iron can block the catalyst pores by forming a dense nodular 'glassy' shell on the catalyst surface. This shell inhibits diffusion of both feed into the catalyst and products exiting the catalyst. Before the start of the trial, the Ecat was examined under a scanning electron microscope and iron nodules were observed. In addition to limiting diffusion, these nodules often negatively impact catalyst fluidisation properties and decrease the apparent bulk density (ABD).

Burnaby had been using flushing Ecat to mitigate feed vanadium and iron effects. Flushing Ecat addition rate often exceeded fresh catalyst addition rate. The refinery carried out several catalyst reformulations over the years that allowed it to operate under these high metal conditions.

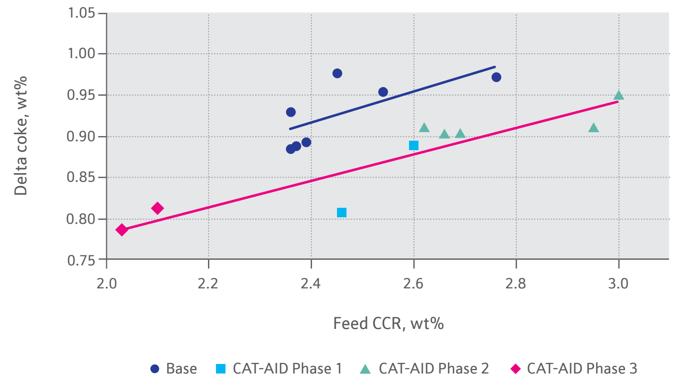

Figure 1: Reduced delta coke

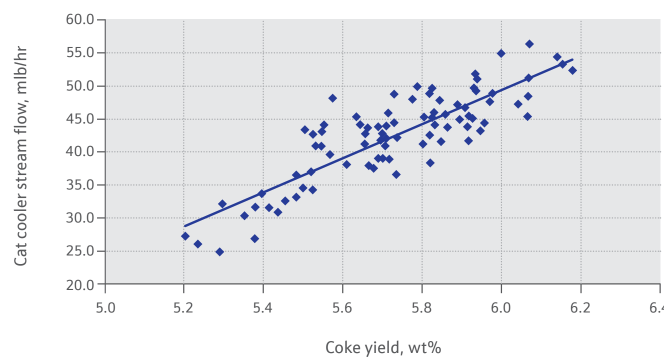

Figure 2: Coke yield primarily controlled by catalyst cooler duty

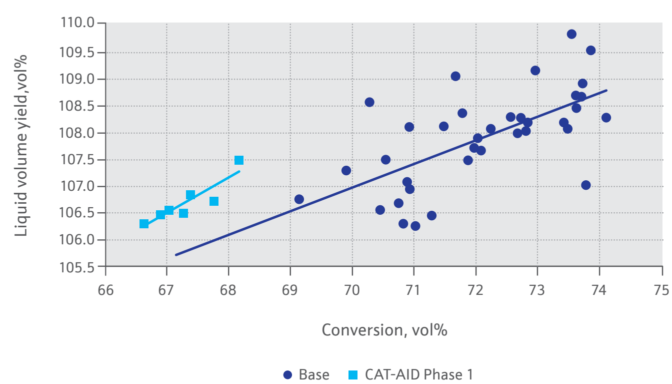

Figure 3: Increased liquid volume yield

Trial

Prior to the commercial trial, advanced catalytic evaluation (ACE) testing was conducted with Burnaby feed and Ecat. The separate particle metals trapping additive, **CAT-AID**™, showed positive results.

The primary trial goal was to lower catalyst operating expenses by reducing fresh catalyst, flushing Ecat addition, and SOX additive usage.

The trial was conducted in three phases after the 10 wt% base load of the additive was completed.

- **Phase 1:** evaluate the savings from reduced fresh catalyst additions, this lasted for 12 days.
- **Phase 2:** maintain constant catalyst addition rates with lower feed quality, this lasted for 15 days.
- **Phase 3:** evaluate the savings from reduced flushing Ecat additions, this lasted for 53 days.

For all three phases, the additive concentration in unit inventory was 9 – 10 wt%. The **CAT-AID** addition rate was significantly lower in the third phase due to the reduction in flushing Ecat addition rate.

Phase 1

During the first phase, the fresh feed rate to the unit was reduced from 17 300 bpd base down to 15 600 bpd due to other refinery objectives. The riser temperature normally varies between 960 – 970 °F and it remained in this range for phase 1. Regenerator temperature was held relatively constant by adjusting catalyst cooler duty. Ecat iron stayed at the base levels of 0.86 to 0.91 wt%, Ecat vanadium increased during the period from 7000 ppm to 8300 ppm, and nickel increased from 3200 ppm to 3600 ppm.

Overall, operating conditions during the first phase of the trial were close to base case levels with the exception of the reduced charge rate. Phase 1 was successful. Fresh catalyst addition rate was reduced from 2.8 tpd to 1.8 tpd. Delta coke was reduced by 0.06 wt% reducing catalyst cooler duty. The lower catalyst cooler duty reduced coke yield by 0.3 wt% and the SOX additive addition rate was also reduced from 420 lb/d to 30 lb/d.

Phase 2

During the second phase of the trial, feed quality was reduced while maintaining near constant catalyst addition rate. Feed nitrogen increased by 11%, Conradson Carbon Residue (CCR) increased from 2.5 to 2.8 wt%, and feed vanadium increased by 12%.

Despite the decrease in feed quality, conversion stayed the same at constant riser outlet temperature. Delta coke and coke yield also remained constant. This phase of the trial demonstrates the flexibility provided by **CAT-AID**, which prevented delta coke, coke yield, and catalyst cooler duty from increasing. Without the additive, the catalyst addition rate would have been increased to mitigate the effects of lower feed quality. Conversion and product yields would have deteriorated as well. During this portion of the trial, SOX additive addition was stopped completely and SOX emissions remained below the limit.

Phase 3

The purpose of this trial phase was to reduce flushing Ecat addition rate. During this period, feed quality to the unit improved slightly from the base case. Feed nitrogen was reduced by 7%, feed CCR was reduced from 2.5 to 2.2 wt%, and feed vanadium was lowered by 16%.

The catalyst to oil (cat/oil) ratio was reduced by increasing feed temperature and decreasing riser outlet temperature. Feed temperature was increased from 477 to 508 °F, and riser outlet temperature was decreased from 966 to 962 °F. Both changes significantly affect conversion, making the results of this portion of the trial less obvious. Previous Burnaby data analysis has shown that a 10 °F change in riser temperature shifts conversion by 2.5 vol.%.

The major success in this phase was reducing flushing Ecat by 60% and fresh catalyst by 7%. With the reduction in flushing Ecat, circulating Ecat vanadium and nickel both increased during this portion of the trial. Corrected conversion reduced by 1.4 vol.%. This is significant because the major change in feed temperature, riser temperature, and reduction in flushing and fresh catalyst should have resulted in a much greater loss of conversion. However, the **CAT-AID** contribution to the catalyst system ensured this conversion loss did not occur.

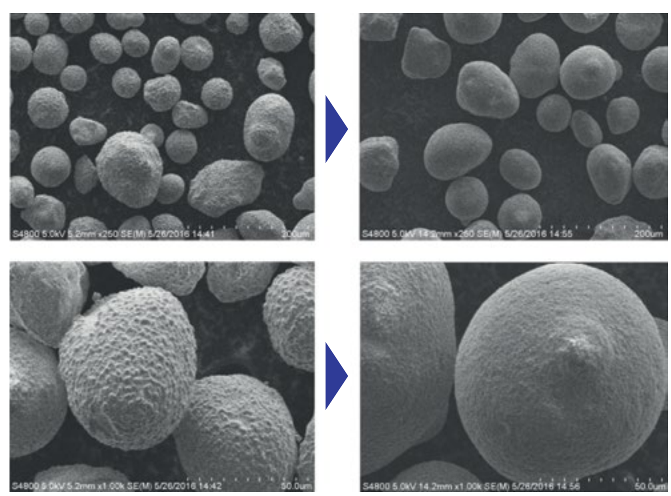

Figure 4: Reduced iron nodules. Without **CAT-AID** (left); with **CAT-AID**, 36 days after trial begins (right).

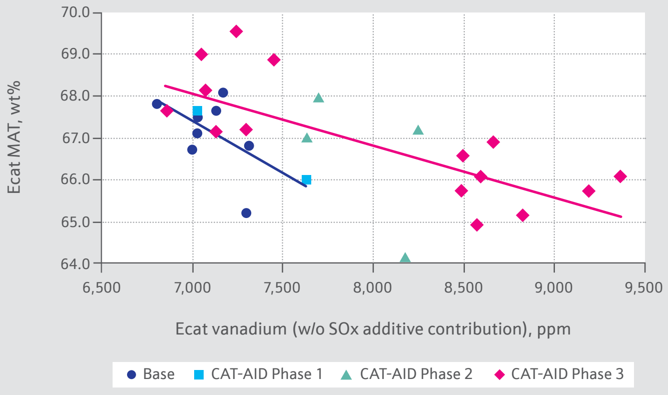

Figure 5: Increased vanadium tolerance.

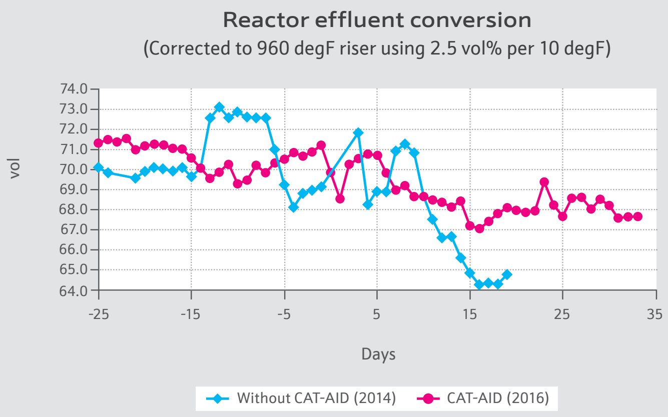

Figure 6: Improved activity retention.

Overall results

Each phase of the trial showed the positive impact of the metals trapping technology. The ability to reduce fresh catalyst addition, lower feed quality, and reduce flushing Ecat addition all have obvious impacts on operational flexibility. Although each phase was conducted with a separate goal, common benefits were observed during all three phases.

Delta coke reduction

Feed contaminants result in increased delta coke. Since **CAT-AID** mitigates the impact of both vanadium and iron poisoning, delta coke is reduced. At Burnaby, delta coke was reduced by an average of 0.08 wt% (Figure 1).

The refinery operates a catalyst cooler in its FCC regenerator. The catalyst cooler duty is adjusted to maintain a constant regenerator temperature. This is an unconventional operation as regenerator temperature is generally allowed to vary. Feed and riser temperatures are also relatively steady, which in turn maintains a constant cat/oil ratio of approximately 6.3. At constant cat/oil, a reduction in delta coke will show up as a direct reduction in coke yield. The reduction in coke yield at constant feed quality is 0.51 wt% of feed.

Coke yield = delta coke × cat/oil

Base case: coke yield = 0.95 wt% × 6.3 = 5.99 wt%

CAT-AID trial: coke yield = 0.87 wt% × 6.3 = 5.48 wt%

The heat balance and coke yield are dependent on catalyst cooler duty:

- The additive reduced delta coke.
- Lower delta coke required lower catalyst cooler duty at constant regenerator temperature.
- Lower catalyst cooler duty reduced coke yield (Figure 2).

For the 0.51 wt% coke yield reduction, the catalyst cooler steam production was reduced by 13 000 lb/hr. The lower catalyst duty allows more operational flexibility and reduces dependence on the catalyst cooler for stable FCC operation. The negative of reducing catalyst cooler duty is that additional steam generation is required elsewhere in the refinery. The net benefit is that 13 000 lb/hr of steam will be generated with inexpensive natural gas rather than high value liquid FCC feed.

Liquid volume yield increase

Coke yield has a direct effect on liquid volume yield. Figure 3 shows a clear increase in liquid volume yield of 0.8 vol.% when **CAT-AID** was cross checked against it. Based on the coke yield reduction of 0.51 wt%, the expected liquid volume increase is 0.6 vol.%. Additionally, the additive reduces dry gas yield. The total liquid yield increase of 0.8 vol.% is comprised of 0.6 vol.% from coke yield reduction and 0.2 vol.% from dry gas reduction.

Iron poisoning impacts

Prior to beginning the trial, iron nodules were observed on Burnaby's Ecat. The iron poisoning inhibits hydrocarbon molecules from diffusing into and out of the catalyst pores. After the additive was well established in the FCC, Ecat was examined again under a scanning electron microscope. A clearly visible difference was observed on the catalyst at equal iron levels of 0.9 wt% (Figure 4). The change in surface morphology significantly improves the catalyst selectivity and activity.

Catalyst activity impact

Ecat Micro Activity Test (MAT) activity increased by 0.5 – 1.0 wt% with **CAT-AID** due to mitigation of vanadium and iron poisoning. Figure 5 shows MAT activity as a function of Ecat vanadium comparing base case and trial data. Activity is strongly dependent on Ecat vanadium level, which is observed in almost all FCC units. The metals trap reduces the deactivation of the base catalyst by subjecting it to less contaminant metals.

SOX additive reduction

The magnesium component of the technology allows it to act similarly to a SOX additive. As a result, Burnaby was able to discontinue SOX additive additions. Even though **CAT-AID** does not have as high of an efficiency as a normal SOX additive, its addition rate was higher than the SOX additive. Therefore, the refinery was able to increase SOX reduction and discontinue SOX additive addition.

Reduction in fresh catalyst and flushing Ecat

One of the primary goals of the trial was to reduce fresh catalyst and flushing Ecat addition rates. Assessing the effects of reducing flushing Ecat additions is not easy. However, in 2014, flushing Ecat was discontinued for 20 days and this data can be used for comparison purposes. The previous decline in conversion is shown in Figure 6 compared with the data from phase 3 of the trial. The conversion decline without **CAT-AID** was two to three times greater than with the additive. There is optimisation required between fresh catalyst and flushing Ecat addition rate and it will be dependent on feed type and operating goals.

Conclusion

The additive greatly increased profitability and operational flexibility at Parkland Burnaby. The trial resulted in a decrease in delta coke of 0.08 wt% allowing for lower catalyst cooler duty and lower coke yield. Liquid volume yield was increased by

0.8 vol.% due to lower coke and lower dry gas yields. Feed quality was decreased at constant conversion. An increase in metals tolerance was achieved with Ecat MAT activity increasing by 0.5 – 1.0 wt% at constant Ecat vanadium. Iron nodules on the catalyst have been mitigated to help improve catalyst activity and selectivity. Fresh catalyst and flushing Ecat addition rates were reduced. Lastly, SOX additive has been reduced to zero with emissions well below target. Recently, Parkland has been able to operate without its catalyst cooler online and use **CAT-AID** to increase crude rate. Normally, it would not be able to operate and maintain rate without the cooler.

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